Determination of Closed Pore Content in Nanoporous Films by SANS Contrast Match

Ronald C. Hedden,[1] Barry J. Bauer,[1] Hae-Jeong Lee,[1] and Wen-li Wu,[1]

[1]Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899

INTRODUCTION

Much of the recent developmental efforts in low-k dielectrics involve production of nanoporous thin films. By using synthetic techniques that leave nanometer-sized (< 5 nm) pores in the dielectric, the resultant dielectric constant can be reduced to unprecedented levels. The nanoporosity not only lowers the average dielectric constant, but changes the strength, permeability, and other crucial properties of the films. Therefore, it is necessary to characterize the nature of the porosity to guide the synthetic efforts and to correlate a variety of electrical and mechanical properties.

The National Institute of Standards and Technology (NIST) Polymers Division has developed a method of measuring pore volume fraction, matrix density, pore size, pore connectivity, and coefficient of thermal expansion by using a combination of techniques.[1-2] Small angle neutron scattering (SANS) and x-ray reflectivity (XR) along with atomic composition data from ion scattering produce important information on the films, but cannot provide data on more subtle film characteristics.

A porous thin film can have two distinct types of pores: open (accessible to solvent), or closed (inaccessible to solvent). The wall can be uniform in atomic composition, or have heterogeneities. Recently, NIST has begun SANS contrast match measurements in which a mixture of hydrogen and deuterium containing probe molecules are used to fill the open pores with material of varied neutron contrast. In this way, film characteristics such as closed pore porosity and matrix heterogeneity can be assessed.

CONTRAST MATCH METHODS

The contrast match technique takes advantage of the ability to change the neutron contrast of a solvent by mixing deuterium and hydrogen versions of that solvent.[3] Figure 1 demonstrates the principle of the contrast match method. (In Figure 1, solvent-filled pores are represented by gray circles, unfilled pores by white circles, and wall density fluctuations by black circles.) When the sample is exposed to the saturated solvent vapor, the open pores are filled, and their neutron contrast changes. The neutron contrast of (unfilled) closed pores and of the wall material remain the same. The SANS intensity is proportional to the difference in the contrast factors, s, squared, where, r is the mass density, n_i is the molar content, b_i is the scattering length, and m_i is the molar mass of component i.

$$I(q) \propto (r_w s_w - r_s s_s)^2, s = \sum_i n_i b_i \Big/ \sum_i n_i m_i \quad (1)$$

Therefore, for any q value of the SANS intensity, a series of solvent mixtures with varied contrast can be used with equation (1) to calculate the solvent composition at which the SANS intensity goes to a minimum. The calculated s and the atomic composition are then used to calculate the wall density. At the contrast match point, the only contrasting areas will be closed pores and wall heterogeneities. Any remaining coherent scattering intensity results from the closed pores and/or the heterogeneous wall. If no coherent SANS signal is present at the match point, then only a negligible amount of these features are present.

A significant difficulty with contrast matching is that any mixture of hydrogen-containing solvent produces a q-independent incoherent background, complicating data analysis. If the sample cell is filled with liquid solvent, excess solvent fills the gaps between the films, creating substantial incoherent scattering. The method employed herein uses saturated solvent vapor instead of liquid. Pores are filled with liquid by capillary condensation, but external solvent is eliminated, decreasing the incoherent scattering to acceptable levels.

Samples. Two nanoporous thin film samples were obtained from International Sematech (Xerogel* and XLK™*). Atomic composition from ion scattering and film thickness from x-ray reflectivity were obtained previously as described elsewhere.[1-2]

Small Angle Neutron Scattering. SANS measurements were conducted at the NIST Center for Cold Neutron Research 8m facility (Gaithersburg, MD).[4] Data were analyzed by established methods with the software provided by the Center for Neutron Research at NIST.[5] The uncertainties in the scattering data are calculated as the estimated standard deviation of the mean. The total combined uncertainty is not given, as comparisons are made with data obtained under the same conditions. In cases where the limits are smaller than the plotted symbols, the limits are left out for clarity. Films were enclosed in a vacuum-tight flow cell with quartz windows. Scattering from (5 to 10) identical films was simultaneously measured to increase the coherent scattering intensity. The sample cell was placed in a vacuum chamber to minimize scattering from air. Toluene-h8 and toluene-d8 (saturated vapors in air) were delivered to the flow cell using two syringe pumps equipped with 100 cc syringes. Each syringe contained a small amount of liquid toluene in equilibrium with its saturated vapor. The effluent from the syringes was combined and delivered to the flow cell.
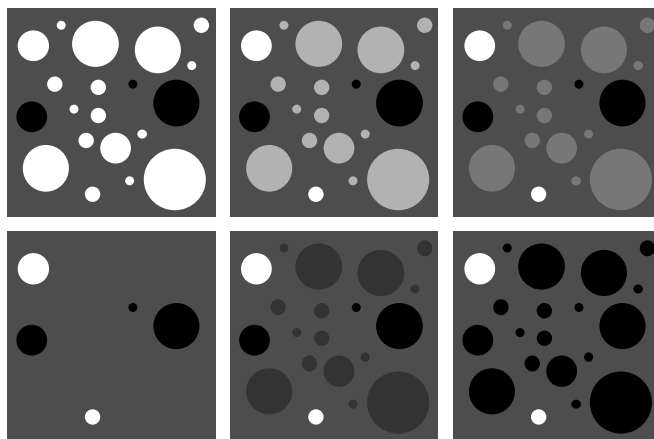

Figure 1. Schematic representation of neutron contrast in a porous thin film as pores are filled will solvent mixtures of varying contrast (increasing from upper left to lower right). Only open pore contrast changes with filling. At the contrast match point (lower left), only closed pores (white) or wall heterogeneities (black) are seen.

RESULTS AND DISCUSSION

Figure 2 shows SANS data for the Xerogel* film sample. For data shown in the figures, the relative uncertainty in the composition of the solvent mixture is ± 1 % of the quoted values, based on the researchers' experience with the equipment. Scattering was measured in air and in saturated toluene vapor of varying deuterium content. I(q) for this sample was consistent with scattering from random two-phase structures as described by Debye, Anderson, and Brumberger.[6] The SANS intensity was maximum for pores filled with 100 % toluene-d8 and decreased as the h content increased until a toluene mixture of about (20:80) d8:h8 by volume was reached. The SANS intensity increased for 100 % toluene-h. The air scattering was higher since the contrast factor for air is equivalent

to a –15 % deuterium content. A match point of (14 ± 1) % toluene-d8 by volume was calculated from equation (1) by a fit to all of the SANS curves.

A wall mass density of ρ_w=(1.37 ± 0.07) g / cm^3 was calculated from equation (1). A toluene mixture of the match-point composition was then used to fill the pores and additional SANS data were taken. The lowest curve of figure 1 is the SANS intensity multiplied by a factor of 25 to emphasize the weak intensity.

At the match point, little coherent scattering remains, indicating qualitatively that few closed pores and wall inhomogeneities are present. The volume fraction of closed pores and/or wall heterogeneities can be estimated by fitting I(q) data at the match point to the Debye equation.[6]

$$I(q) = \frac{8\pi\, f(1-f)(r_w s_w - r_s s_s)^2 x^3}{(1+x^2 q^2)^2} \qquad (2)$$

Figure 3 shows the match point scattering data and several fits to the Debye equation. ξ is a correlation length related to the average dimension of the scattering domains, and ϕ is the volume fraction of the scattering domains. Relative uncertainties in calculated ξ and ϕ are ± 10 % of the quoted values, based on the researchers' experience with the methods. Choosing physically reasonable values for the correlation length, the upturn in the data at low q can only be fitted to the Debye equation for $\phi \approx$ .0001. We therefore conclude that this sample essentially consists of uniform walls with open pores.

Figure 4 shows SANS data for the XLK^{TM} film sample. The shape of the I(q) vs. q data is not consistent with the random two-phase model of Debye, et al.[6] The upturn in scattering intensity at low q indicates that this sample contains some excess large scattering entities compared to a random mixture. In this case, scattering intensity passes through a minimum at a toluene composition of about (40:60) % d8:h8 by volume. The upturn at low q is still present at the match point, indicating that the sample has wall heterogeneities and/or closed pores. Further experiments are necessary to determine whether the residual scattering results from wall density fluctuations or closed pores. However, a population of large closed pores seems inconsistent with a population of smaller open pores. Therefore, a certain amount of wall heterogeneities seems likely. The match point (40 ± 2) % toluene-d8 by volume was calculated from equation (1) by a fit to all of the SANS curves. The calculated wall mass density for this sample was (2.09 ± 0.10) g / cm^3.

CONCLUSIONS

Small-angle neutron scattering contrast-match experiments are sensitive to closed pores and wall inhomogeneities in porous thin films. The contrast-match technique permits calculation of the film wall density. For films with homogeneous walls, application of the Debye random two-phase model to match-point scattering data quantifies the volume fraction of closed pores. With an appropriate model, SANS data is useful to analyze structures of more complex low-k dielectrics with inhomogeneous walls.

ACKNOWLEDGEMENTS

REFERENCES

1. Wu, W.-L., Wallace, W.E.; Lin, E.K.; Lynn, G.W.; Glinka, C.J.; Ryan, E.T.; Ho, H.M. *J. Appl. Phys.* **2000**, *87:3*, 1193-1200.
2. Bauer, B.J.; Lin, E.K.; Lee, H.J.; Wang, H.; Wu, W.-L. *J. Electron. Mater.* **2001**, *30:4*, 304-308.
3. *Polymers and Neutron Scattering*, Higgins, J. S.; Benoit, H. C., Claredon Press: Oxford, 1994.
4. Prask, H.J.; Rowe, J.M.; Rush, J.J.; Schröder, I.G.J. *Res. Natl. Inst.Stand. Technol.* **1993**, *98*, 1.
5. Hammouda, B.; Krueger, S.; Glinka, C.J. *Res. Natl. Inst. Stand. Technol.* **1993**, *98*, 31.
6. Debye, P., Anderson, H.R., and Brumberger, H. *J. Appl. Phys.* **1957** *28*, 679.
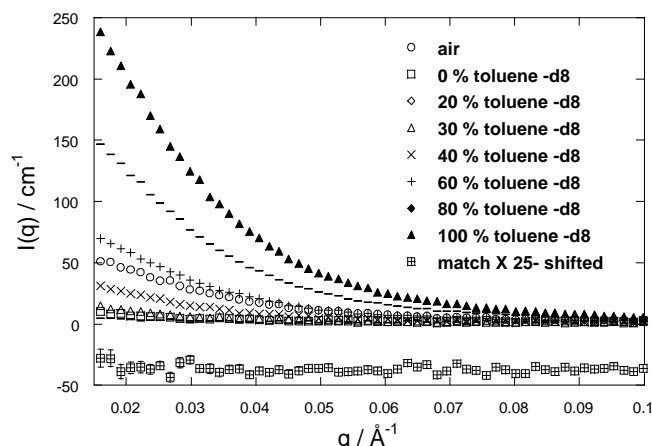

Figure 2. SANS contrast match for Xerogel thin film for various toluene-d8/toluene-h8 mixtures. Bottom line is match point, shifted for clarity and expanded X 25 in intensity.
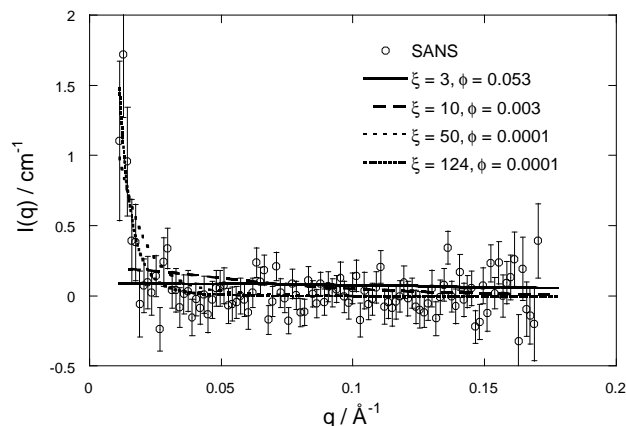

Figure 3. Match-point scattering for Xerogel sample. Fits are to the Debye equation (eqn. 2).
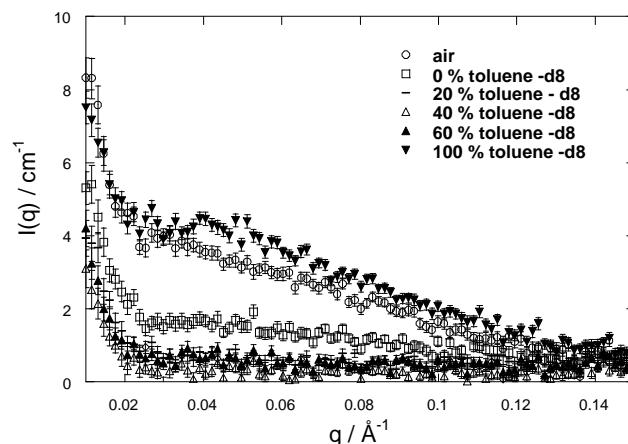

Figure 4. SANS contrast match for XLK^{TM} thin film for various toluene-d8/toluene-h8 mixtures.